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LETTERS TO THE EDITOR

Dedicated to V. F. Mironov on His 60th Anniversary

Synthesis, Acid-Base and Complexing Properties of *N*,*N*,*N*',*N*'-Tetrakis(*O*-butylhydroxyphosphorylmethyl)-1,2-diaminoethane

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Abstract—A method of synthesis of organophosphorus analog of ethylenediaminetetraacetic acid (a common complexon), *N,N,N',N'*-tetrakis(*O*-butylhydroxyphosphorylmethyl)-1,2-diaminoethane, has been elaborated. The product structure has been elucidated by means of NMR spectroscopy and X-ray diffraction analysis. Constants of the acid dissociation and the stability of the 1 : 1 complexes with Co(II), Ni(II), and Cu(II) ions have been determined.

Keywords: organophosphorus complexon, acid-base properties, complex stability constant

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We have earlier synthesized an organophosphorus analog of nitrilotriacetic acid (a common complexon), potassium salt of aminotris(*O*-butylmethylphosphonic) acid [1], and studied its acid-base properties as well as the complex formation with certain doubly charged transition metals cations [2, 3]. We have revealed that this triphosphorylated amine is significantly different from nitrilotriacetic acid in the complex formation, yielding weaker complexes.

In this study, we suggested a method for the synthesis of an organophosphorus analog of another complexon widely used in analytical and coordination chemistry (ethylenediaminetetraacetic acid EDTA): *N*,*N*,*N*',*N*'-tetrakis(*O*-butylhydroxyphosphorylmethyl)-1,2-diaminoethane **4**. On top of that, acid-base and complex-forming properties of the latter were investigated. The interaction of 1,3,6,8-tetraazatricyclododecane (synthesized via α-condensation of formaldehyde with ethylenediamine [4]) afforded earlier unknown *N*,*N*,*N*',*N*'-tetrakis(butoxymethyl)ethane-1,2-diamine **1**. The reaction of the latter with 4 eq. of dibutyl phosphonate led to the formation of the tetraphosphorylated diamine **2** (with almost quantitative yield, ^{31}P NMR monitoring) that was transformed without purification into readily crystallizing tetrapotassium salt **3** via hydrolysis with potassium hydroxide. The addition of nitric acid to a solution of salt **3** gave acid **4** (Scheme 1).

According to X-ray diffraction data, acid **4** existed in the crystal in the form of zwitterion salt: both nitrogen atoms were protonated and two hydroxy groups at the phosphorus atom were deprotonated (Fig. 1). The negative charge was localized at the O^3 and $O^{3'}$ oxygen atoms, the bond lengths in the deprotonated phosphorus-containing moiety being P^1–O^3 1.516(2), P^1–O^1 1.466(2), and P^1–O^2 1.575(2) Å and those in the other phosphoryl fragment being P^2–O^4 1.480(2), P^2–O^5 1.510(2), and P^2–O^6 1.585(2) Å. The molecule was centrosymmetrical, being in a special position of the *P*-1 space group. The N–C bonds were in the *gauche* positions with respect to the phosphoryl groups. The orientation of butyl substituents was different: that at the P^1 atom was *gauche*-oriented with respect to the phosphoryl bond, whereas the alkyl group at the P^2 atom was *trans*-oriented.